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POLAROGRAPHIC REDUCTION BEHAVIOUR AND ANALYSIS OF CYHALOTHRIN IN AGRICULTURAL FORMULATIONS

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ABSTRACT

D.C. polarography, cyclic voltammetry (CV) and differential pulse polarography (DPP) techniques are used to carried out the reduction behaviour analysis of Pyrithroid insecticide Cyhalothrin, in the universal buffer (Britton-Robinson buffer) pH range from 2.0 to 12.0. DPP method for quantitative determination of Cyhalothrin in the concentration range from 1.0×10^{-5} M to 3.0×10^{-8} M and with a lower detection limit of 2.8×10^{-8} M. CV studies signifies that the electrode process was irreversible and adsorption controlled. The number of electrons was calculated and the reduction mechanism was proposed. Kinetic parameters such as transfer coefficient, diffusion coefficient and heterogeneous forward rate constant are evaluated and reported. Differential pulse polarography has been developed for the quantitative estimation of Cyhalothrin in various agricultural formulations using standard addition method.

Keywords: Cyhalothrin, Polarography, Mechanism, Analysis, Agricultural Formulations

INTRODUCTION

Pyrethroids are highly effective insecticides used for the control of a wide spectrum of insect pests, in agriculture, public areas and household **[1]**. The fate of synthetic pyrethroids is very important from a toxicological point of view due to their persistence in the field and also due to their relative bio-accumulation **[2, 3]**. **Figure 1**

Cyhalothrin [Cyano (3-Phenoxyphenyl) methyl-3-(2-chloro-3, 3, 3-trifluoroprop-1-enyl)-2, 2-dimethyl-cyclopropanecarboxylate] is an insecticide in the pyrethroid chemical family. These halogenated and lipophilic synthetic pyrethroids are used worldwide in agricultural, domestic and veterinary applications and recognised as potent neurotoxicants, characterised by high insecticidal properties and low mammalian toxicity **[4]**.

Analysis of various Pyrethroid insecticide compounds was determined in water, soil and vegetables by various analytical methods **[5, 6]**. The reports obtained with pulse techniques have increased the range of practical applications of polarography by assisting the determinations of electroactive species at lower concentrations **[7-9]**. Therefore, the development of a sensitive, convenient and economical electro analytical method is required for the analysis of pyrithroid residues in agricultural formulations.

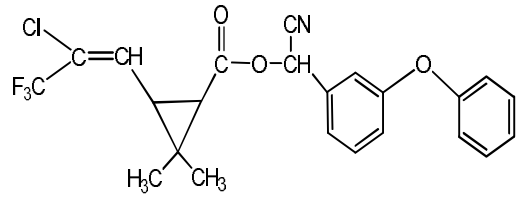

Figure 1: Structure of Chyalothrin

Cyhalothrin is a synthetic pyrethroid insecticide and is widely used for the control of many common pests on crops and domestic animals, which acts as a neuro-poison interfering in the ionic conductance of membranes by prolonging the sodium current **[10, 11]**. It is also used as agropesticide in onion cultivations **[12]**. In addition pyrethroids increase the spontaneous release of neuro transmitters such as dopamine or noradrenaline and may also acts as harmone disruptor **[13]**. Collectively, the facts suggests that cyhalothrin may disrupt male reproduction function. In the present studies the following olefinic group containing pyrithroid insecticides, Cyhalothrin was chosen to carry out the electrochemical reduction behaviour and to develop a sensitive electroanalytical procedure for their analysis in different agricultural formulations.

MATERIALS AND METHODS

A Metrohm unit: E 506 polarecord coupled with E 612 VA-scanner, E 648 VA-combistand, E 608 VA-controller, and a digital electronics 2000 X-Y/t recorder are used for cyclic voltammetric and differential pulse polarographic measurements. All the electrochemical measurements are carried out with three-electrode design at 25 ± 0.1^0C. The DME (area: 0.0223 cm^2, flow rate of Hg: 2.73 mg/sec, and mercury column height: 35 cm) and HMDE (with an area of 0.0328 cm^2) are used as working electrodes. Ag/AgCl(s),Cl^- electrode is used as reference electrode for

cyclic voltammetry and differential pulse polarography. Platinum electrode is used as counter electrode for both the techniques. A modified cell with mercury pool cathode, SCE, platinum wire gauze electrode, and spot galvanometer, was used for controlled potential electrolysis.

Cyhalothrin was obtained from Ciba - Geigy (India) Ltd., Mumbai. The purity of the sample was tested by melting point determination and TLC analysis. Britton-Robinson buffers of pH 2.0 to 12.0 were prepared by using 0.2 M boric acid, 0.05 M citric acid, and 0.1 M trisodium orthophosphate. All the chemicals used are of pure analar grade. Stock solution of Cyhalothrin was prepared by dissolving the required amount in methanol and making up to volume with the supporting electrolyte to obtain the desired concentration. Before running the voltammograms the test solution was purged with purified nitrogen for 10 min. A 0.02% aqueous solution of Triton X-100 was used to eliminate the polarographic maxima.

A standard stock solution (1.5×10^{-3} M) of the compound was prepared by the dissolution of the appropriate amount of the Cyhalothrin pesticide in double distilled water. A 10 ml of the solution (9 ml of the supporting electrolyte + 1 ml of unknown concentration of the depolarizer) is transferred into a polarographic cell and polarogram is recorded after complete deaeration for 15 min. After obtaining the polarogram, small increments (0.2 ml) of the standard solution of electroactive species is added to the cell, deaerated for 1 min. and the polarogram is again recorded under similar conditions. In the same manner, 10 polarograms are recorded for 10 standard additions. The amount of unknown species is calculated by using relevant equation. In the present study the best conditions are obtained at pH 2.0 with a drop time 2 sec, a pulse amplitude 50 mV and applied potentials of -1.02 V for Cyhalothrin. The relative standard deviations and correlation coefficients are found to be 1.21% and 0.963.

RESULTS AND DISCUSSION

Characterization of Wave/Peak

Figures 2-4 explains the electrochemical behaviour of Cyhalothrin over the pH range from 2.0 to 12.0. A single well defined wave/peak in the entire pH range was obtained, and it is attributed to the reduction of the olefinic group (>C=C<) to the corresponding saturated product in a two electron process.

Nature of the Electrode Process

The diffusion controlled adsorption free nature of the electrode process was evidenced

from the linear plots of i_d vs.$h^{1/2}$ **(Figure 5)** passing through origin in all the supporting electrolytes ranging from pH 2.0 to 12.0. The experimental constancy $i_p/v^{1/2}$ with scan rate (v) in cyclic voltammetry indicates that the electrode process is free from any kinetic complications.

The reduction process was found to be a diffusion controlled irreversible process in the entire buffer system studied, as evidenced from the disobedience of Tomes' criterion, log-plot analysis and dependence of $E_{1/2}$ with the concentration of electroactive species in d.c. polarography, the absence of anodic peak in the reverse direction and the variation of peak potential with scan rate in cyclic voltammetry. The marginal variation of peak potential (E_m) with concentration and nonlinearity in the plots of $i_m$vs.$1-\sigma$ / $1+\sigma$ in differential pulse polarography also confirms the irreversible nature of the electrode process.

The half-wave and peak potentials are seen to have shifted towards more negative potentials with increase in pH of the buffer solution indicating the participation of protons in the reduction process of Cyhalothrin. The number of protons involved in the rate determining step is calculated from $E_{1/2}$ vs. pH plots and is found to be one for the experimental compound Cyhalothrin in the reduction processes.

Identification of the Products

Comparison of wave heights of Cyhalothrin in millicoulometry has indicated the number of electrons involved in the electrode process as two in acidic (pH 2.0) and basic media (pH 12.0). Controlled potential electrolysis is carried out with mercury pool cathode,saturated calomel electrode as reference electrode and platinum wire electrode as counter electrode. About 50 mg of the electroactive species under investigation is dissolved in a minimum amount of methanol and added to the cell containing supporting electrolyte (pH 4.0). The applied potentials are fixed at -0.45 V for Cyhalothrin. The electrolysis is carried out approximately for 4 hrs. The product formed after controlled potential electrolysis is identified as the corresponding saturated derivative of olefinic group (>C=C<) by IR spectral studies (absence of C=C stretching absorption band at 1685cm^{-1}.

Kinetic Date

The typical kinetic parameters of the electrode process calculated at various pH values in different techniques are presented in **Tables 1 to 3**. The adsorption free nature of the electrode process is clearly evidenced from the nearly equal diffusion coefficients values obtained from all the techniques for Cyhalothrin. The diffusion coefficient values

are seen to decrease gradually, which account for the decrease in diffusion current with increase in pH due to less availability of protons.

The rate constant values obtained for the reduction of olefinic group in acidic medium from all the techniques are found to be high indicating that the rate of reaction is fast in acidic solutions due to the fact that the involvement of protons is high. In basic medium, the reduction process does not easily occur owing to the less availability of protons. Therefore, lower rate constant values are obtained.

Electrode Mechanism (Figure 6)

Based on the above results and observations obtained in the present investigation, as well as from the literature **[14, 15]**, the following reduction mechanism may be proposed for the Cyhalothrinin the entire pH range:

ANALYSIS

In the present investigation differential pulse polarography has been employed to work out analytical procedures for the estimation of Cyhalothrin in agricultural formulations using both calibration and standard addition methods. The determined compounds are found to exhibit well resolved peaks in pH 4.0 and are chosen for quantitative studies. The peak currents are found to vary linearly with the concentration ofthe depolariser over the concentration range 1.0×10^{-5}M to 3.0×10^{-8}M for Cyhalothrin. The lower detection limits are found to be 2.8×10^{-8}M for the respective compound, which are calculated from the expression dl = 3Sd /m where dl is the lower detection limit, Sd is the standard deviation and m is the slop of the calibration plot.

Recommended Analytical Procedure

The standard stock solution (1×10^{-3}M) of both the compounds is prepared by dissolving the required quantity of the electroactive species in methanol. 1ml of the standard solution is transferred into a polarographic cell and made up with 9 ml of the supporting electrolyte and the solution is purged with oxygen free nitrogen gas for 10 min. After recording the polarograms, small increments (0.2 ml standard solution) are added and the polarograms are recorded after each addition under similar conditions. The optimum conditions for the analytical determination of Cyhalothrin in pH 4.0 are found to be a drop time 2 sec, pulse amplitude 50 mV and applied potentials of -0.40 V. The relative standard deviations and correlation coefficients for 10 replicates are found to be 1.56% and 0.991 for Cyhalothrin. This method is successfully employed for the determination of the compound in different agricultural formulations.

In the present analysis, different agricultural formulations Karate, Flectron and Sipirin of Cyhalothrin are chosen. The required quantity of formulations corresponding to a stock solution of concentratio 1×10^{-3} M is accurately measured and transferred into a 100 ml calibrated flask containing 50 ml of Methanol. A solution of 1×10^{-5} M is prepared by diluting this stock solution with the buffer solution and the above described procedure was employed. Assay results for the selected formulations are given in **Table 4**.

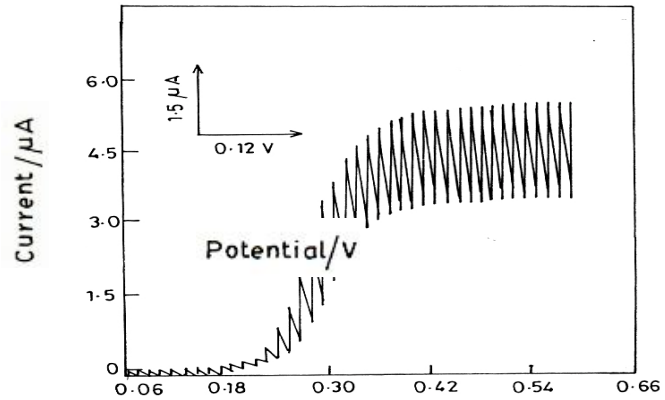

Figure 2: Typical D.C. Polarogram of Cyhalothrin in pH 2.0; Concentration: 0.5 mM, Drop Time: 3 Sec

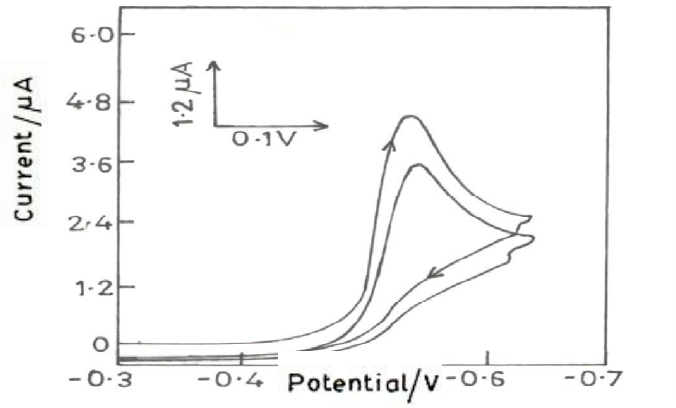

Figure 3: Typical Cyclicvoltammogram of Cyhalothrin in pH 6.0; Concentration : 0.5 mM, Scane Rate: 40 mVs^{-1}

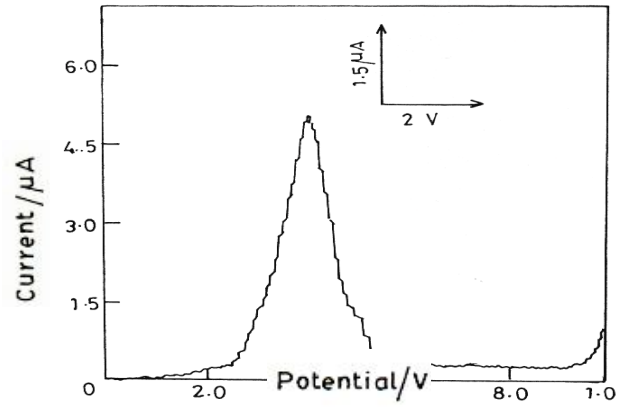

Figure 4: Typical Differential Pulse Polarogram of Cyhalothrin in pH 4.0; Concentration: 0.5 mM, Drop Time: 2 Sec, Pulse Amplitude : 50 mV

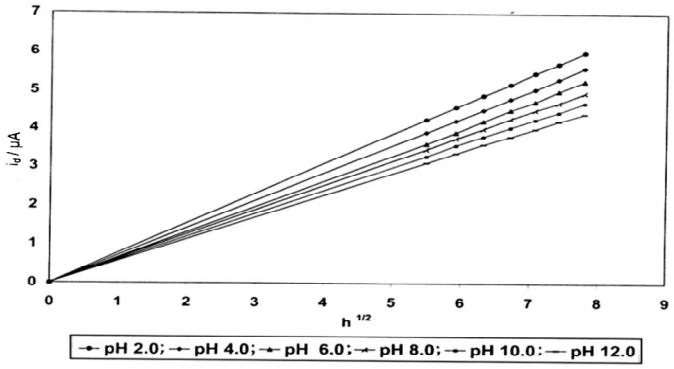

Figure 5: $i_d$vs. $h^{1/2}$ Plots of Cyhalothrin, Concentration : 0.5 mM

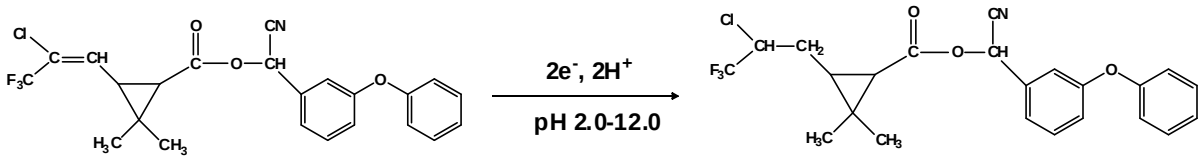

Figure 6: Electrode Mechanism of Cyhalothrin

Table 1: Typical d.c. Polarographic Data of Cyhalothrin Concentration: 0.5 mM, Drop Time: 3 Sec

pH	$\frac{-E_{1/2}}{V}$	$\frac{i_d}{\mu A}$	αn_a	$\frac{D\times10^6}{cm^2\,s^{-1}}$	$\frac{k^0_{f,h}}{cm\,s^{-1}}$
2.0	**0.29**	**5.2**	**0.68**	**4.97**	**2.37×10^{-9}**
4.0	**0.42**	**4.9**	**0.69**	**3.92**	**5.49×10^{-10}**
6.0	**0.51**	**4.5**	**0.61**	**3.62**	**1.33×10^{-11}**
8.0	**0.64**	**4.4**	**0.53**	**3.40**	**2.89×10^{-13}**
10.0	**0.76**	**4.0**	**0.43**	**3.26**	**8.81×10^{-15}**
12.0	**0.85**	**3.9**	**0.45**	**2.02**	**6.11×10^{-18}**

Table 2: Typical Cyclic Voltammetric Data of Cyhalothrin Concentration: 0.5 mM, Drop time: 3 Sec, Scanerate: 40 mVs^{-1}

pH	$\frac{-E_p}{V}$	$\frac{i_p}{\mu A}$	αn_a	$\frac{D\times10^6}{cm^2\,s^{-1}}$	$\frac{k^0_{f,h}}{cm\,s^{-1}}$
2.0	**0.31**	**5.1**	**0.61**	**4.88**	**8.43×10^{-9}**
4.0	**0.43**	**4.8**	**0.64**	**3.98**	**5.75×10^{-11}**
6.0	**0.53**	**4.6**	**0.62**	**3.56**	**1.81×10^{-12}**
8.0	**0.67**	**4.1**	**0.59**	**3.42**	**2.94×10^{-13}**
10.0	**0.76**	**3.9**	**0.51**	**3.36**	**9.33×10^{-15}**
12.0	**0.85**	**3.7**	**0.46**	**3.01**	**1.25×10^{-18}**

Table 3: Typical Differential Pulse Polarographicdata of Cyhalothrin Concentration: 0.5 mM, Drop Time: 2 Sec, Pulse Amplitude: 50 mV

pH	$\frac{-E_m}{V}$	$\frac{i_m}{\mu A}$	αn_a	$\frac{D\times10^6}{cm^2\,s^{-1}}$	$\frac{k^0_{f,h}}{cm\,s^{-1}}$
2.0	**0.27**	**5.5**	**0.71**	**4.92**	**4.87×10^{-4}**
4.0	**0.40**	**5.1**	**0.63**	**4.14**	**2.53×10^{-9}**
6.0	**0.49**	**4.7**	**0.65**	**3.92**	**5.45×10^{-10}**
8.0	**0.60**	**4.4**	**0.52**	**3.81**	**6.95×10^{-12}**
10.0	**0.69**	**4.1**	**0.54**	**3.21**	**2.33×10^{-14}**
12.0	**0.81**	**3.8**	**0.41**	**2.97**	**5.28×10^{-17}**

Table 4: Determination of Cyhalothrinin Agricultural Formulations in pH 4.0 Pulse Amplitude: 50 mV, Drop Time: 1.4 Sec

Sample	Labelled amount(mg)	Amount found*(mg ± SD)	Average recovery(%)
Karate	**50**	**49.90 ± 0.014**	**99.82**
Flectron	**50**	**49.80 ± 0.017**	**99.61**
Sipirin	**50**	**49.50 ± 0.015**	**99.03**
Karate	**100**	**199.50 ± 0.013**	**99.75**
Flectron	**100**	**199.89 ± 0.018**	**99.89**
Sipirin	**100**	**199.00 ± 0.023**	**99.52**

***Each Value is an Average of Four Determinations**

CONCLUSION

The work describes the voltammetric behaviour of Cyhalothrin based on the reduction of olefinc group at dropping mercury electrode and hanging mercury drop electrode. The result shows that differential pulse polarography is a simple, reliable and inexpensive method for the determination of Cyhalothrin in formulations. The main advantage of the proposed method over the other ones is that the excipients do not interfere and a separation procedure is not necessary. Differential pulse polarography is employed for the analysis of the title compound. Analytical procedures are described for quantitative estimation of the compound in agricultural formulations using both standard addition and calibration

methods. The detection limits are found to be 10^{-8} M levels for both the compounds

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REFERENCES

[1] Oudou HC, Alonso RM and Hansen HCB, Voltammetric behaviour of the synthetic pyrethroid lambda-cyhalothrin and its determination in soil and well water, Analytica Chimica Acta., 523, 2004, 69.

[2] Oudou HC and Hansen HCB, Sorption of lambda-cyhalothrin, cypermethrin, deltamethrin and fenvalerate to quartz, corundum, kaolinite and montmorillonite Chemospherie., 49, 2002, 1285.

[3] Velmunegan B, Ambrose T and Selvanayagam M, Genotoxic evaluation of lambda-cyhalothrin in Mystusgulio, J. Environ. Biol., 27, 2006, 247.

[4] Leng G and Gries W, Simultaneous determination of pyrithroidmetabolities in human urine by gas chromatography-high resolution mass spectrometry, J. Chromatogr. B., 814, 2005, 285.12p\

[5] Leng G, Grives W and Selim S, Biomarker of pyrethrum exposure, ToxicolLett., 162, 2005, 195.

[6] Thriveni T, Kumar JR, Lee JY and Sreedhar NY, Electrochemical Determination of Phenothrin in Agricultural Formulations, Vegetables, and Storage Bags of Wheat and Rice by Differential Pulse Adsorptive Stripping Voltammetry (DP-AdSV), Food Anal. Methods., 2, 2009, 66.

[7] Coomber DC, Tucker DJ, Bond AM, Electrochemical reduction of Pyrethroid insecticides in Non-aqueous solvents, J. of Electroanalytical Chem., 63, 1997, 426,

[8] Sreedhar M, Reddy MT, Balaji K and Reddy JS, Electrochemical reduction behaviour of the synthetic pyrethroid insecticide Cyfluthrin and its determination in formulations and environmental samples, Int. J. of Environ. Analytical Chem., 86 (10), 2005, 757-756.

[9] Clark JM, Insecticides as tools in probing vital receptors and enzymes in

the nervous system, Pesticide and Biochem. Physiol., 57, 1997, 225-254.

[10] Gao H, Ling Y, Xu T, Jing H and Sheng W, Development of an Enzyme-Linked Immunosorbent Assay for the Pyrethroid Insecticide Cyhalothrin, J. Agricultural and Food Chem., 54, 2006, 5284.

[11] Ratnasooriya WD, Ratnayake SSK and Jayanthunga YNA, Effects of pyrethroid insecticide ICON (lambda cyhalothrin) on reproductive competence of male rats, Asian J. Androl., 4, 2002, 35.

[12] Garey J, Wolff MS and Beatriz GT, Estrogenic and anti-progestagenic activities of pyrethroids insecticides, Environ. Health Product., 107, 1999, 173.

[13] Subbalakskmamma M and Reddy SJ, Electrochemical reduction behavior and analysis of some organophosphorous pesticides, Electroanalysis, 6, 1994, 521.

[14] Sreedhar NY, Reddy PRK, Reddy GVS and Reddy SJ, Differential pulse polarographic determination of dicrotophos, crotoxyphos and chlorfenvinphos in grains and soils, Talanta, 14, 1997, 1859.